Resonance absorber based on thin films of pseudoisocyanine J-aggregates

R V Markov, Z M Ivanova, A I Plekhanov, N A Orlova, V V Shelkovnikov

Abstract. **Nanometre films of pseudoisocyanine N-alkyl-substituted J-aggregates are obtained on glass substrates by spin-coating from organic dye solutions. The optical and non-linear optical properties of these films are investigated. These films are shown to possess a high optical quality over the area of size more than 30×30 mm and a high photochemical stability. These films feature strong absorption saturation at the maximum of excitonic absorption of the aggregates. The radiative damage threshold of the films at the maximum of the excitonic absorption was measured to be 5 MW cm^{-2}. The dispersion of optical nonlinearity of the films within the J-band is measured by the Z-scan and probe field methods. The films can be used as two-dimensional optical light-controlled switches.**

Keywords: *thin films, J-aggregates, cubic susceptibility.*

1. Introduction

Future information networks that will provide the bit rate of the order of 1 Tbit s^{-1} require fast subpicosecond-response optical switches. Such signal demultiplexers can be based on inorganic semiconductors [1–3]. It was proposed in paper [4] to use a fibre device with the negative and positive dispersion for demultiplexing picosecond solitons. It was shown recently [5] that by using a thin film of squiryl dye J-aggregates, terahertz demultiplexing of light signals can be performed by transforming a train of femtosecond pulses (with a pulse repetition rate of 1 THz) into spatially separated beams. Films used in two-dimensional optical switches should possess along with a large and fast-response optical nonlinearity a high optical quality over a large area of several tens of square millimetres.

R V Markov, A I Plekhanov Institute of Automatics and Electrometry, Siberian Branch, Russian Academy of Sciences, prosp. akad. Koptyuga 1, 630090 Novosibirsk, Russia; tel. (3832) 333 174;
e-mail: fractal@iae.nsk.su; web-site: http//www.iae.nsk.su
Z M Ivanova, N A Orlova, V V Shelkovnikov N N Vorontsov Novosibirsk Institute of Organic Chemistry, Siberian Branch, Russian Academy of Sciences, prosp. akad. Lavrent'eva 9, Novosibirsk, Russia; tel. (3832) 343 996; e-mail: vsh@nioch.nnc.ru

In this paper, we studied nanometre J-aggregate films that we prepared by spin-coating from solutions of new synthesised substituted cyanine dyes. The films are stable at room temperature and have good optical quality over the area of 30×30 mm.

2. Preparation of J-aggregate films and their optical properties

We prepared J-aggregate films using the dye 1,1$'$-diethyl-2,2$'$-cyanine iodide [pseudoisocyanine (PIC)]. The specific feature of J-aggregates is a new narrow absorption band, which appears upon aggregation of dye molecules at 585 nm (J-band) and is shifted to the red relative to the 550-nm absorption band of monomers. J-aggregates can represent elongated threadlike structures [6–8] or micelles [9]. Such macroaggregates contain up to ten thousands of dye molecules.

The optical properties of molecular aggregates differ from those of individual molecules and crystals. Because of the dipole–dipole coupling, the optical excitation of an individual molecule can transfer to other molecules in aggregates, i.e., the excitation becomes delocalised. Since the excited states of J-aggregates are collective states, they are characterised by a high optical nonlinearity ($\chi^{(3)} \sim 10^{-7}-10^{-8}$ CGS units [10–13]).

For practical applications of J-aggregates, stable and well reproducible samples are required. At present there exist the methods for producing J-aggregates in aqueous solutions, frozen glasses and polymer matrices [6]. However, these methods do not give stable aggregates. The production of films without a stabilising polymer can lead to an increase in the concentration of J-aggregates in a layer, resulting in an increase in the optical nonlinearity of the film. Thin films with the enhanced concentration of J-aggregates obtained for the first time in paper [14] featured a high optical nonlinearity $\chi^{(3)} \sim 10^{-5}$ CGS units, however, J-aggregates proved to be unstable and were destroyed due to crystallisation for 1–2 days.

We stabilised J-aggregates in paper [14] by using PIC with long N-alkyl substituents. This approach is based on the assumption that J-aggregates are formed like micelles of cationic surfactants [15]. A change in the substituent length does not change the optical properties of an individual molecule, but the substituent length affects the mutual arrangement of molecules in the J-aggregate. In this way, we can affect the ability of the dye to form molecular aggregates and change its structure [16].

In this paper, we studied PIC with a series of symmetric [$C_2H_5 - C_2H_5$ (1a), $C_6H_{13} - C_6H_{13}$ (ab), $C_{10}H_{21}C_{10}H_{21}$ (ac), $C_{15}H_{31} - C_{15}H_{31}$, (1d), $C_{18}H_{37} - C_{18}H_{37}$ (1e)] and asymmetric [$C_2H_5 - C_6H_{13}$ (2a), $C_2H_5 - C_{10}H_{21}$ (2b), $C_2H_5 - C_{15}H_{31}$ (2c), $C_2H_5 - C_{18}H_{37}$ (2d)] N-alkyl substituents [17]. The absorption spectra of PIC with substituents 1a–1e and 2a–2d in organic solutions at concentrations below 10^{-3} mol L^{-1} were identical, which shows the length of the N-alkyl substituent has no effect on the optical properties of an individual molecule.

The dye films were deposited on glass substrates of size 30×30 mm by spin-coating from organic dye solutions (acetonitrile or ethilenedichloride). The J-band was not observed in PIC films with substituents 1c–1e. As the length of the alkyl substituent was increased, the so-called H-aggregates were formed in the film, which are characterised by a broad exciton band shifted to the blue with respect to the absorption band of dye monomers.

Experiments showed that J-aggregates are formed in the films only for PIC with N-alkyl substituents 1a, 1b, 2a–2d. As the length of substituents 2a–2d increases, the tendency to a spontaneous formation of J-aggregates is revealed, which is caused by a more efficient transformation of monomers to aggregates. This was well manifested when the films were prepared from solutions with a low dye concentration (Fig. 1). In this case, PIC with substituent 2b did not produce aggregates, whereas PIC with substituents 2c and 2d gives aggregates, the J-band for PIC with substituent 2d being more intense. The characteristic width of the J-bands was ~ 230 cm^{-1}, being virtually the same for all aggregates studied.
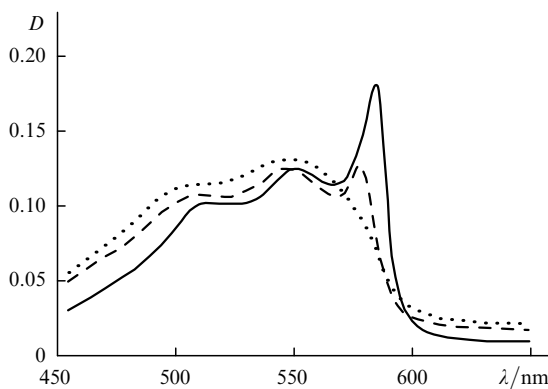

Figure 1. Dependences of the optical density D of J-aggregate films on the wavelength λ for PIC with substituents 2b (dotted curve), 2c (dashed curve), and 2d (solid curve). Films were obtained from the acetonitrile solution at the dye concentration of 10^{-3} mol L^{-1}. The centrifuging rate was 3000 rpm.

The J-aggregate films of PIC with alkyl substituents 2b–2d are more stable than those of PIC with substituent 1a. They persist at room temperature for a long time (more than half year). The J-band intensity gradually increases during the film storage. This process becomes noticeable with increasing the relative humidity of the air. When the films were kept in the humid atmosphere for three days and over, the ratio of the optical density of the J-band to the optical density of the monomer absorption band increased approximately by 50 %. In this case, the J-band shifted to the blue on the average by 4 nm, depending on the substituent

length. Such spectral behaviour of the J-band was observed for J-aggregate films of PIC with substituents 2b–2d. This effect can be explained by the hydrophobic properties of the dye, which are enhanced with the length of the alkyl substituent.

We studied the optical and nonlinear optical properties of stable J-aggregate films of PIC with alkyl substituents 2a–2d. We found that the J-band of J-aggregates of PIC with substituent 2a is located in the region 578–579 nm, while the J-band of J-aggregates of PIC with substituent 2d is shifted to the region 585–587 nm. The J-band of J-aggregates of PIC with substituents 2b, 2c lies between these regions, its position being dependent on the conditions of film deposition. Assuming that the shift of the J-band in the exciton model for one-dimensional aggregates is determined by the energy of dipole–dipole interaction of adjacent molecules in the J-aggregate [18], this behaviour of the J-band can be explained by the modification of the geometrical structure of the J-aggregate resulting in the change in the energy of dipole–dipole interaction between neighbouring molecules in the J-aggregate.

3. Structure of thin films of J-aggregates

Recent achievements in atomic force microscopy (AFM) allow the *in situ* observation of the J-aggregate structure. Such studies, which revealed the intense J-band, were performed for J-aggregate films of PIC with substituent 2d. Fig. 2 shows the AFM image of the film that was prepared on a glass substrate by spin-coating from the dye solution. One can see that J-aggregates represent randomly located cigar-shaped structures. Their average size varies from 80 to 110 nm in length, from 40 to 60 nm in width, and from 6 to 12 nm in height. These structures differ from threadlike structures that were observed earlier using near-field microscopy [7]. They also differ from island leaf-shaped structures observed at the interface of the aqueous solution of PIC chloride and mica [19]. The cigar-shaped structures appear probably due to adhesion of threadlike micelles forming multilayer band-shaped micelles. Such a process is known in the literature and was described for paired cationic N-alkyl surfactants [20].
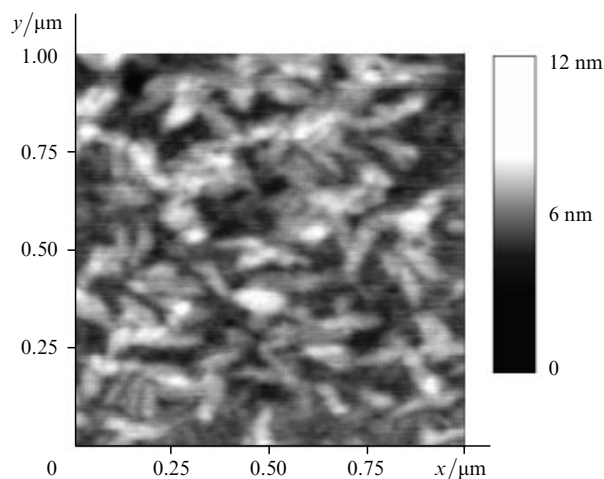

Figure 2. AFM image (of size 1×1 μm) of the J-aggregate film of PIC with substituent 2d.

4. Dispersion of optical constants of J-aggregate films

The values of optical constants (dispersion of the complex refractive index $n = n_0 - ik$) of J-aggregate films are needed in their various applications. The optical constants of thin films can be measured by the methods of photometry, polarimetry, and ellipsometry [21–24]. We used ellipsometry. The dispersion of the optical constants of films and their thickness were measured with a spectral ellipsometer developed at the Institute of Semiconductor Physics, Siberian Division, RAS [25].

We measured the dispersion of the refractive index and of the absorption coefficient of thin films deposited onto a silicon substrate or a fused silica substrate. When films were measured on silica substrates, the reflection from the pure substrate surface was eliminated by placing a black paper with the immersion liquid.

The film thickness was measured by the methods of AFM microscopy and spectral ellipsometry. We used in our calculations the film thickness determined by the ellipsometry method. The error of measurements of the refractive index and the absorption coefficient was ±0.01, and the film thickness was measured with an accuracy of 0.5 nm. The dispersion dependences of the refractive index and the absorption coefficient for J-aggregate films of PIC with substituent 2d are shown in Fig. 3. These dependences for films with other J-aggregates are similar. In the long-wavelength region, where the film is transparent, the normal dispersion was observed (Fig. 3a). In the range from 500 to 570 nm, the anomalous dispersion was observed, which is maximal in the J-band. It is interesting that the refractive index of the film in this spectral region greatly exceeds the refractive indices of fused silica and optical glass.
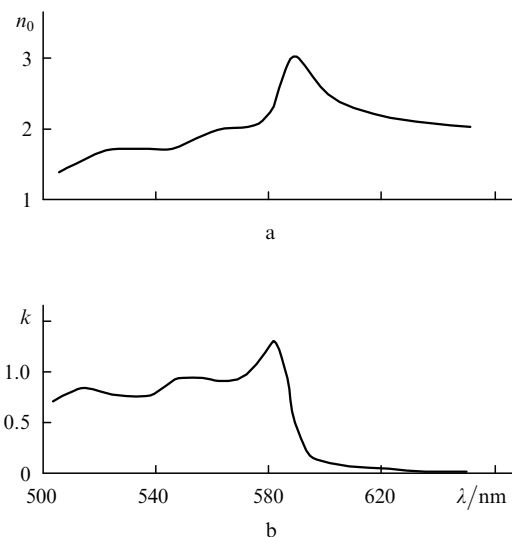

Figure 3. Dependences of the real (a) and imaginary (b) parts of the refractive index on the wavelength for the J-aggregate film of PIC with substituent 2d on a silicon substrate. The film thickness is 16 nm.

The absorption coefficient of J-aggregate films is shown in Fig. 3b. The 584.5-nm absorption band is the J-band. The absorption coefficient at the maximum of this band is $\alpha_0 = 4\pi k/\lambda \sim 2.4 \times 10^5$ cm^{-1}.

5. Dispersion of nonlinear susceptibility of J-aggregate films

We studied a series of ~ 30-nm thick J-aggregate films with substituents 2b–2d by the Z-scan [26, 27] and probe field methods. The measurements were performed at room temperature at the approximately constant air humidity. We found that the change in the absorption coefficient α of the films was proportional to the radiation-pulse intensity up to $I \simeq 2$ MW cm^{-2} (we used nanosecond pulses). At higher intensities, the saturation appeared, and for $I \simeq 5$ MW $\times$ cm^{-2} the films were burnt. The unsaturated nonlinear absorption coefficients β of the films under study were virtually identical and were equal approximately to -0.025 cm W^{-1} at the maximum (β was determined from the relation $\alpha = \alpha_0 + \beta I$). This value of β corresponds to Im$\chi^{(3)} = \beta\lambda cn_0^2/(640\pi^3) = -1.3 \times 10^{-5}$ CGS units, where $c = 3 \times 10^8$ m s^{-1} is the speed of light, $n_0 = 2.5$, and λ is the wavelength of light in vacuum in metres. It was shown in papers [6, 12, 28] that the relaxation time of optical nonlinearity of PIC J-aggregates was less than 1 ps.

Measurements of β performed by the z-scan method showed that the absorption coefficient changed most strongly near the J-band, the change being caused by nonlinear bleaching of the sample. However, we found that the bleaching band could shift to the blue by 1.4–2.0 nm when the radiation intensity was changed. The characteristic dispersion dependence $\chi^{(3)}(\lambda)$ is shown in Fig. 4. One can see that Im $\chi^{(3)}(\lambda)$ contains a small positive part along with a great negative part. The induced darkening band is shifted to the Stokes region by $\sim 4.4 - 5.5$ nm with respect to the J-band. The intensity of the former band increases with increasing radiation intensity.
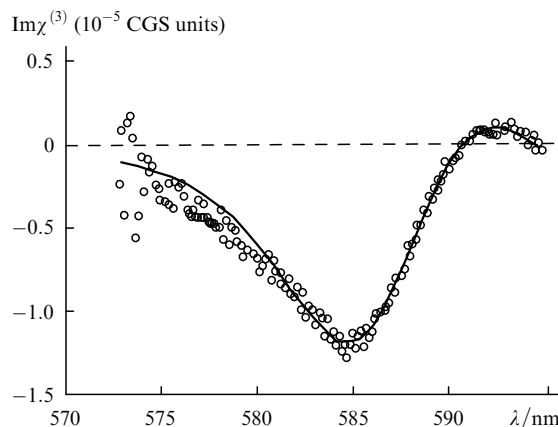

Figure 4. Dispersion Im $\chi^{(3)}(\lambda)$ for the J-aggregate film of PIC with substituent 2d. The circles are experimental data; the solid curve is the dependence obtained by fitting within the framework of the four-level model using expression (5) from paper [27].

The observed spectral dependences of the nonlinear absorption spectrum (in particular, nonlinear darkening observed to the red with respect to the J-band) cannot be explained by the two-level model of J-aggregates. The necessity of consideration of other transitions in J-aggregates was pointed out by many authors [28–30].

The features of the nonlinear absorption spectrum can be explained using a four-level model of exciton transitions

in aggregates [27]. The bleaching is attributed to the absorption saturation at the transition from the ground excitonic state to the first excited state. The population relaxation occurs both to the ground state and the lower-lying state. Comparison of the theoretical curve calculated by expression (5) from paper [27] by fitting with the experimental dependence shows good agreement between the theory and experiment (Fig. 4). Our experimental results show that the bleaching band for J-aggregates of PIC with substituents 2c and 2d is narrower than predicted by the model of saturation of a homogeneously broadened transition. The induced darkening band can be related to the exciton–exciton interaction [31].

6. Conclusions

Our study of synthesised PIC with N-alkyl substituents has shown that the substituent length affects the structure and stability of a molecular aggregate. We have found that stable J-aggregates can form submicron films only for PIC with long asymmetric substituents. We determined the dispersion of the refractive index and of the absorption coefficient of stable J-aggregate films. We also measured the value and dispersion of the imaginary part of cubic susceptibility for J-aggregate films. At the bleaching maximum of the J-band, the imaginary part of cubic susceptibility was approximately 10^{-5} CGS units for the film thickness much lower than the wavelength of light. The experimental spectral dependence $\mathrm{Im}\,\chi^{(3)}(\lambda)$ is well described by the four-level model of excitonic transitions in the aggregate.

References

1. Nakamura S, Ueno Y, Tajima K *IEEE Photon. Technol. Lett.* **11** 1575 (1998)
2. Kobayashi H, Takahashi R, Matsuoka Y, Iwamura H *Electron. Lett.* **34** 908 (1998)
3. Yeo D H, Yoon K H, Kim H R, Kim S J *IEEE J. Quantum Electron.* **37** 824 (2001)
4. Melo A M, Lima J L S, Sombra A S B *Opt. Commun.* **186** 87 (2000)
5. Furuki M, Tian M, Sato Y, Pu L S *Appl. Phys. Lett.* **77** 427 (2000)
6. Kobayashi T *J-aggregates* (Singapore: World Science Publ., 1966) p. 227
7. Higgins D A, Barbara P F *J. Phys. Chem.* **99** 3 (1995)
8. Kobayashi T, Misawa K *J. Lumin.* **72** 38 (1997)
9. Sugiyma S, Yao H, Matsuoka O, Kawabata R, Kitamura N, Yamamoto S *Chem. Lett.* **1** 37 (1999)
10. Wang Y J *Opt. Soc. Am. B: Opt. Phys.* **8** 981 (1991)
11. Bogdanov V A, Viktorova E N, Kulya SV, et al. *Pis'ma Zh. Eksp. Teor. Fiz.* **53** 100 (1992)
12. Zhuravlev F A, Orlova N A, Shelkovnikov V V, et al. *Pis'ma Zh. Eksp. Teor. Fiz.* **56** 264 (1992)
13. Gadonas R, Feller K-H, Pugzlys A *Opt. Commun.* **112** 157 (1994)
14. Shelkovnikov V V, Zhuravlev F A, Orlova N A, Plekhanov A I *J. Mater, Chem.* **5** 1331 (1995)
15. Pavlik A, Kirstein S, De Rossi U, Daehne S *J. Phys. Chem.* **101** 5646 (1997)
16. De Rossi U, Moll J, Spieles M, et al. *J. Pract. Chem.* **337** 203 (1995)
17. Orlova N A, Kolchina E F, Zhuravlev F A, et al. *J. Heterocycl. Comp.* (to be published)
18. McRae E G, Kasha M, in *Physical Processes in Radiation Biology* (New York: Academic Press, 1964)
19. Sugiyama S, Yao H, Matsuoka O, Kawabata R, Kitamura N, Yamamoto S *Chem. Lett.* **1** 37 (1999)
20. Oda R, Huc I, Homo J -C, et al. *Langmuir* **15** 2384 (1999)
21. Heavens O S *Optical Properties of Thin Solid Films* (New York: Dover, 1991)
22. Abeles F *Prog. Opt.* **2** 251 (1963)
23. Born M, Wolf E *Principles of Optics,* 4th ed. (Oxford: Pergamon Press, 1969; Moscow: Nauka, 1973)
24. Azzam R M A, Bashara N M *Ellipsometry and Polarized Light* (Amsterdam: North-Holland, 1977)
25. Shvets V A, Rykhlinskii S V *Avtometriya* (1) 5 (1997)
26. Sheik-Bahae M, Said A A, Van Stryland E W *Opt. Lett.* **14** 955 (1989)
27. Markov R V, Plekhanov A I, Rautian S G, et al. *Opt. Spektrosk.* **85** 643 (1998)
28. Minoshita K, Taiji M, Misawa K, et al. *Chem. Phys. Lett.* **218** 67 (1994)
29. Spano F C, Mukamel S *Phys. Rev A* **40** 5783 (1989)
30. Knoester J *Phys. Rev. A* **47** 2083 (1993)
31. Markov R V, Plekhanov A I, Shelkovnikov V V, Knoester J *Phys. Stat. Sol.* **221** 529 (2000)